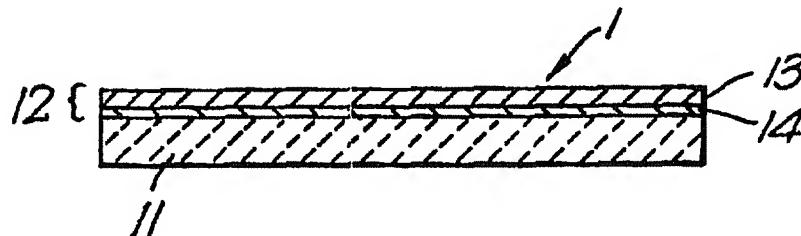




INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification 6 : C03C 17/34		A1	(11) International Publication Number: WO 98/11031 (43) International Publication Date: 19 March 1998 (19.03.98)
(21) International Application Number: PCT/GB97/02433	(81) Designated States: AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, GH, HU, ID, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZW, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).		
(22) International Filing Date: 10 September 1997 (10.09.97)			
(30) Priority Data: 9619134.1 13 September 1996 (13.09.96) GB			
(71) Applicant (for all designated States except US): PILKINGTON PLC [GB/GB]; Prescot Road, St Helens, Merseyside WA10 3TT (GB).			
(72) Inventors; and		Published	
(75) Inventors/Applicants (for US only): GALLEGOS, José, Manuel [GB/GB]; 22 Ellerbrook Drive, Lathom, Ormskirk, Lancashire L40 5SZ (GB). SIDDLE, John, Robert [GB/GB]; 25 Knowsley Road, Southport, Merseyside PR9 0HW (GB).		With international search report.	
(74) Agent: HALLIWELL, Anthony, Charles; Pilkington plc., Group Patents Dept., Pilkington Technology Centre, Hall Lane, Lathom, Ormskirk, Lancashire L40 5UF (GB).			

(54) Title: COATED GLASS



(57) Abstract

A high performance solar control glass comprises a glass substrate with a coating comprising a heat absorbing layer and a low emissivity layer of a metal oxide. Preferred heat absorbing layers absorb preferentially at wavelengths above 700 nm, and may be, for example, of non-stoichiometric or doped tungsten oxide, or of cobalt oxide, chromium oxide, iron oxide or vanadium oxide. Preferred low emissivity layers are of semi-conductor metal oxide, for example doped tin oxide or doped indium oxide. Because of the nature of the layers, the coatings may be of neutral colour and be suitable for deposition on-line on the glass ribbon, during the glass production process, by pyrolytic methods for example chemical vapour deposition.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

COATED GLASS

The invention relates to coated glass, and in particular to high performance solar control coated glass.

There is an increasing demand for solar control glasses, especially high performance solar control glasses that exhibit a neutral colour in both reflection and transmission. By "high performance" solar control glasses we mean glasses which transmit a significantly higher percentage of incident light than of total incident radiation energy (total solar heat). Body tinted glasses containing added iron are capable of providing high solar control performance, but the iron tends to tint the glass green, and a green tint is not always acceptable. Inclusion of further additives, for example, a combination of selenium and a metal oxide such as cobalt oxide, can convert the green tint to a more neutral colour, but at the cost of some loss of performance i.e. with an increase in the proportion of incident heat : incident light transmitted. Coatings incorporating silver layers in combination with appropriate dielectric layers in multilayer stacks can provide high performance solar control products, close to neutral in both reflection and transmission, but have significant disadvantages. First, suitable silver layers are not susceptible to on-line deposition methods in which the coating is applied to the hot glass ribbon as it is produced i.e. before it is cut and removed from the production line, but are applied by off-line low pressure techniques such as magnetron sputtering. Second, such silver coatings have limited physical durability requiring careful protection and handling during processing, and protection of the coated glass in the final product, for example, by glazing in a multiple glazing unit with the coating facing the airspace of the unit.

It would be desirable to have a coating which would provide a high performance solar control glazing without the disadvantages of the silver coatings referred to above, and which preferably would have a near neutral colour in reflection and transmission, or at least provide an alternative to the green reflection and transmission colours characteristic of the high performance body tinted glasses referred to above.

According to the present invention there is provided a high performance solar control coated glass comprising a glass substrate and a coating comprising a heat absorbing layer and a low emissivity layer comprising a metal compound.

The invention is illustrated but not limited by the accompanying diagrammatic drawings in which:-

Figure 1 shows a section through a coated glass in accordance with one embodiment of the invention.

Figure 2 shows a section through a coated glass in accordance with a second preferred embodiment of the invention.

Figure 3 shows a section through a double glazing unit incorporating a coated glass as illustrated in Figure 1.

Referring to Figure 1, a high performance solar control coated glass 1 comprises a glass substrate 11, preferably of clear float glass, and a coating 12 comprising a heat absorbing layer 14 and a low emissivity layer 13 of a metal compound.

The embodiment shown in Figure 2 is similar to the embodiment of Figure 1, with a coated glass 2 comprising a glass substrate 21, preferably of clear float glass, and a coating 22. However, coating 22 differs from coating 12 in that it comprises, in addition to heat absorbing layer 24 and low emissivity layer 23, an iridescence suppressing underlayer 25 as further discussed hereinafter.

Figure 3 illustrates the coated glass pane 1 of Figure 1 assembled in parallel spaced relationship with a second pane of glazing material 31, typically of clear float glass, the panes being spaced apart and sealed together by spacing and sealing system 32, to form double glazing unit 3 having airspace 33. The coating 12 faces the airspace 33 of the unit.

To enhance the performance, it is desirable that the heat absorbing layer of the coating absorbs preferentially at wavelengths above 700 nm; preferably, it is substantially non-absorbing in the visible region of the spectrum. The heat absorbing layer may be a substantially transparent conductive oxide layer, with tungsten oxide being preferred in view of the characteristic absorption peak it exhibits around 900 nm.

Tungsten oxide exists in both conductive and dielectric forms. Stoichiometric tungsten oxide, WO_3 , is a dielectric, being substantially non-absorbing in the near infra red.

Non-stoichiometric tungsten oxide, WO_{3-x} , where x is typically up to about 0.03 (preferably in the range 0.005 to 0.025), and doped tungsten oxide, containing an appropriate dopant of different valency, for example, hydrogen, fluorine, an alkali metal, copper, silver or gold are conductive and suitable for use in the practice of the present invention.

A tungsten oxide layer used as a heat absorbing layer may be crystalline or amorphous. If crystalline, it is generally preferred to avoid too large a crystal size as large crystals are liable to result in the appearance of haze.

Other heat absorbing materials which may be used to form the heat absorbing layer include other coloured transition metal oxides such as chromium oxide, cobalt oxide, iron oxide, molybdenum oxide, niobium oxide and vanadium oxide; mixtures of such metal oxides may also be used.

The heat absorbing layer will normally have a thickness in the range 50 nm to 500 nm, especially 80 nm to 200 nm.

The low emissivity layer is a layer of a metal compound, normally a metal oxide (as other low emissivity compounds such as metal nitrides and metal silicides tend to have lower light transmissions), and a transparent semiconductor, for example, a doped indium, tin or zinc oxide. Preferred materials include tin doped indium oxide and fluorine doped tin oxide. The low emissivity layer will normally have a thickness in the range 100 nm to 600 nm (as use of a thicker layer is likely to result in an unnecessary reduction in light transmission without sufficient reduction in emissivity to compensate), especially a thickness in the range 200 nm to 500 nm. The low emissivity layer may have an emissivity of less than 0.4 (the numerical values of emissivity referred to in this description and the accompanying claims are values of normal emissivity, measured in accordance with ISO 10292 : 1994, Annex A), although it is preferred to use a low emissivity layer which provides an emissivity of 0.2 or less.

The low emissivity layer of the coating will normally overlie the heat absorbing layer, with the solar control glass glazed with the coating facing towards the interior of the glazed space (usually, but not necessarily, a building).

Use of thin films, as in the present invention, may result in the appearance of interference colours and iridescence. To avoid or at least alleviate undesirable colour resulting from interference effects, a colour suppressing underlayer (which may itself be a combination of sub-layers) may be applied to the glass prior to deposition of the heat absorbing and low emissivity layers. The composition and deposition of such iridescence suppressing underlayers is described in prior published patents including GB 2 031 756B, UK 2 115 315B and EP 0 275 662B. Thus, according to a preferred aspect of the invention, an iridescence suppressing layer or layers is incorporated under the coating comprising a heat absorbing layer and a low emissivity layer.

An additional layer may be incorporated over the coating, for example as an anti-reflection layer, but the use of such overlayers may lead to a loss of the low emissivity properties i.e. an increase in emissivity, and is not usually preferred.

The heat absorbing layer and low emissivity layer of the present invention may be deposited by known techniques, for example by sputtering, including reactive sputtering, or by chemical vapour deposition. Indeed, it is an important advantage of the invention that both the above layers are susceptible to deposition by chemical vapour deposition techniques providing for the possibility of applying the coating to the hot ribbon of glass during the glass production process. Methods of depositing heat absorbing layers by chemical vapour deposition are described, for example, in EP 0 523 877 A1 and EP 0 546 669 B1, while methods of depositing metal oxide low emissivity layers by chemical vapour deposition are described, for example, in GB 2 026 454B and EP 0 365 239B.

The invention is illustrated but not limited by the following Examples. In the Examples, as in the remainder of the description and claims, the visible light transmissions stated are measured using Illuminant C. The total solar heat transmissions stated are determined by weighting with a solar spectral irradiance function (ASTM E87-891) which represents the direct normal radiation incident on a surface at 37° northern latitude (air mass 1.5).

EXAMPLE 1

An iridescence suppressing underlayer, comprising silicon, carbon and oxygen, having a thickness of 65 nm and a refractive index of about 1.7 was applied to a ribbon of 3mm clear float glass as described in EP 0 275 662B.

A glass pane cut from the ribbon was overcoated by conventional reactive magnetron dc sputtering over the underlayer with a heat absorbing tungsten oxide layer about 100 nm thick doped with hydrogen to provide an absorption peak of 70% at a wavelength of 910 nm (when measured on clear 3 mm float glass in the absence of an underlayer).

An indium tin oxide layer about 265 nm thick, serving as a low emissivity layer and exhibiting an electrical resistivity of 4×10^{-4} ohms centimetres, was deposited over the tungsten oxide layer by conventional reactive magnetron dc sputtering using an indium tin target containing 10 atomic percent tin. Such an indium tin oxide layer has an emissivity of about 0.08.

The resulting coated glass pane had the following properties:

Visible light transmission 70.4%

Total solar heat transmission 55.9%

On incorporation of the coated pane into a double glazing unit with a 3 mm pane of uncoated clear float glass and an air space of 12 mm, and with the coating towards the air space, the resulting unit would have a visible light transmission of 64% and a total solar heat transmission of 44%, and exhibit the following reflection and transmission colours under illumination (Illuminant C):

	a*	b*	L*
Reflection	-5.2	-5.1	46
Transmission	-2.9	1.2	84

EXAMPLE 2

An iridescence suppressing underlayer system, comprising an initial layer of undoped tin oxide 25 nm thick and a layer of silica 25 nm thick was applied to a ribbon of clear float glass 3 mm thick.

A glass pane cut from the ribbon was overcoated by conventional reactive magnetron dc sputtering over the underlayer with a heat absorbing tungsten oxide layer doped with lithium about 420 nm thick to provide an absorption peak of 70% at a wavelength of 910 nm (when measured on clear 3 mm float glass in the absence of an underlayer).

An indium tin oxide layer about 85 nm thick, serving as a low emissivity layer and exhibiting an electrical resistivity of 4×10^4 ohms centimetres was deposited over the tungsten oxide layer by conventional reactive magnetron dc sputtering using an indium tin target containing 10 atomic percent tin.

The resulting coated glass pane had the following properties:

Visible light transmision 69%

Total solar heat transmission 54%

On incorporation of the coated pane in to a double glazing unit with a 3 mm pane of uncoated clear float glass and an air space of 12 mm, and with the coating toward the air space, the resulting unit would have a visible light transmission of 63% and a total solar heat transmission of 41% and exhibit the following reflection and transmission colours under illumination (Illuminant C):

	a*	b*	L*
Reflection	-3.6	-3.3	90
Transmission	-9.3	5.1	84

EXAMPLE 3

An iridescence suppressing underlayer as described in Example 2 was applied to a ribbon of float glass 3 mm thick.

A glass pane cut from the ribbon was overcoated with a heat absorbing non-stoichiometric tungsten oxide layer about 104 nm thick by magnetron dc sputtering from an oxide target. The oxidation state of the tungsten in the tungsten oxide was determined to correspond to a tungsten oxide of formula $WO_{2.98}$.

An indium tin oxide layer about 270 nm thick, serving as a low emissivity layer, was deposited over the tungsten oxide layer by conventional reactive magnetron dc sputtering using an indium tin target containing 10 atomic percent tin.

On incorporation of the coated pane in a double glazing unit with a 3 mm pane of uncoated clear float glass and an air space of 12.5 mm and with the coating towards the air space, the resulting unit would have a visible light transmission of 66% and a total solar heat transmission of 46% and exhibit the following reflection and transmission colours under illumination (Illuminant C):

	a*	b*	L*
Reflection	-7.7	2.25	49
Transmission	1.9	0.61	85

EXAMPLES 4 - 9

In each of this series of Examples, the optical properties of coated 3 mm clear float glass, and of a double glazing unit comprising a pane of the coated glass and a pane of 3 mm uncoated clear float glass with an air space of 12.5 mm and the coating towards the air space were computed from the known optical properties of the glass and coating layers. The structure of the coatings and properties of the coated glasses are set out in accompanying Tables 1 and 2.

Table 1

Example	4	5	6
First coating layer	380 nm tungsten oxide ¹	240 nm tungsten oxide ¹	126 nm tungsten oxide ¹
Second coating layer	320 nm fluorine doped tin oxide ²	260 nm ITO ³	300 nm ITO ³
Visible LT of coated pane	74.4%	70.1%	60.1%
Total SHT of coated pane	53.5%	51.2%	49.3%
Emissivity of coated pane	0.12-0.2	0.08	0.07
Visible LT of double glazing unit	66.6%	63.6%	55.0%
Total SHT of double glazing unit	41.8%	41.2%	41.0%
Reflection colour of double glazing unit	a*-8.3, b*5.9, L44	a*0.5, b*1.4, L53	a*-2.3, b*3.2, L56
Transmission of double glazing unit	a*-6.3, b*7.9, L86	a*-6.8, b*8.2, L83	a*-6.4, b*7.6, L72

Table 2

Example	7	8	9
First coating layer	96 nm tungsten oxide ¹	380 nm niobium pentoxide ⁴	240 nm niobium pentoxide ⁴
Second coating layer	300 nm ITO ³	320 nm fluorine doped tin oxide ²	260 nm ITO ³
Visible LT of coated pane	56.3%	71.3%	68.2%
Total SHT of coated pane	45.6%	54.6%	53.1%
Emissivity of coated pane	0.07	0.12-0.2	0.08
Visible LT of double glazing unit	51.3%	64.1%	61.0%
Total SHT of double glazing unit	35.2%	42.7%	42.5%
Reflection colour of double glazing unit	a*-4.3, b*2.1, L59	a*-8.0, b*6.1, L43	a*0.6, b*1.1, L54
Transmission of double glazing unit	a*-5.3, b*6.1, L68	a*-6.4, b*7.3, L87	a*-7.2, b*7.9, L85

¹ properties of dc magnetron sputtered non-stoichiometric tungsten oxide used in computation

² properties of fluorine doped tin oxide coating deposited by chemical vapour deposition in computation

³ properties of dc magnetron sputtered tin doped indium oxide coating with electrical resistivity of $1.8 \times 10^4 \Omega \text{ cm}$ used in computation

⁴ properties of dc magnetron sputtered niobium pentoxide doped with 30% atom of lithium used in computation.

The coatings of the present invention offer important advantages over the prior art. Being suitable for a production by pyrolytic methods (which have the added benefit of lending themselves to application on-line) they can be obtained in highly durable form, reducing the need for special care in handling and processing and opening up the possibility of using the coatings in free standing glazing without the need to protect them within multiple glazing units. In comparison with body tinted glasses, they offer the advantages of being suitable for production by a more flexible technique (coating) applicable without the need to change the composition in the glass melting tank (with the inherent loss of production as the changeover takes place), and avoiding the strong green tints observed with the higher performing body tints.

Moreover, excellent performances may be achieved, with glasses having a visible light transmission of over 67% providing total solar heat transmission of less than 57%. In general, the solar control glazings of the present invention will provide a total solar heat transmission at least 10% less than the visible light transmission, while glazings providing a total solar heat transmission at least 12% below (at least 15% below when the coated glass is used with a pane of clear float glass in a double glazing unit) are readily achievable and preferred.

The preferred coated glasses of the present invention are glasses wherein the coating is such as to exhibit reflection (when viewed from the coated side) and transmission (when applied to clear float glass) colours such that $(a^{*2} + b^{*2})^{1/2}$ is less than 12, especially less than 10. In especially preferred embodiments, at least one of the reflection and/or (preferably and) transmission colours is such that $(a^{*2} + b^{*2})^{1/2}$ is less than 7.

Claims

1. A high performance solar control coated glass comprising a glass substrate with a coating comprising a heat absorbing layer and a low emissivity layer of a metal compound.
2. A coated glass according to claim 1 wherein the heat absorbing layer of the coating absorbs preferentially at wavelengths above 700 nm.
3. A coated glass according to claim 1 wherein the heat absorbing layer of the coating is a metal oxide layer.
4. A coated glass according to claim 1 wherein the heat absorbing layer of the coating is a tungsten oxide layer containing less than the stoichiometric amount of oxygen.
5. A coated glass according to any of claims 1 to 4 wherein the heat absorbing layer of the coating is of tungsten oxide doped with hydrogen.
6. A coated glass according to any of claims 1 to 5 wherein the heat absorbing layer of the coating is of tungsten oxide doped with alkali metal.
7. A coated glass according to any of claims 1 to 5 wherein the heat absorbing layer of the coating is of chromium oxide, cobalt oxide, iron oxide, molybdenum oxide, niobium oxide, vanadium oxide or mixture thereof.
8. A coated glass according to any of the preceding claims wherein the heat absorbing layer of the coating has a thickness in the range 50 to 500 nm.

9. A coated glass according to any of the preceding claims wherein the heat absorbing layer of the coating has a thickness in the range 80 to 200 nm.
10. A coated glass according to any of the preceding claims having an emissivity of less than 0.4.
11. A coated glass according to claim 10 having an emissivity of less than 0.2.
12. A coated glass according to any of the preceding claims in which the low emissivity layer is of semiconductor metal oxide.
13. A coated glass according to claim 12 wherein the semiconductor metal oxide is doped tin oxide or doped indium oxide.
14. A coated glass according to claim 12 or claim 13 wherein the low emissivity layer has a thickness in the range 100nm to 600 nm.
15. A coated glass according to claim 14 wherein the low emissivity layer has a thickness in the range 200 nm to 500 nm.
16. A coated glass according to any of the preceding claims in which the low emissivity layer of the coating overlies the heat absorbing layer.
17. A coated glass according to claim 16 in which the coating additionally comprises an iridescence suppressing layer or layers under the heat absorbing layer.
18. A coated glass according to any of the preceding claims exhibiting a total solar heat transmission at least 10% less than its visible light transmission.

19. A coated glass according to claim 18 exhibiting a visible light transmission of over 67% and a total solar heat transmission of less than 57%.
20. A coated glass according to any of the preceding claims wherein the coating is such as to exhibit reflection (when viewed from the coated side) and/or transmission (when applied to clear float glass) colours which are each such that $(a^{*2} + b^{*2})^{1/2}$ is less than 12.
21. A coated glass according to claim 20 wherein the coating is such as to exhibit a reflection (when viewed from the coated side) and/or a transmission (when applied to clear float glass) colour such that $(a^{*2} + b^{*2})^{1/2}$ is less than 7.
22. A high performance solar control coated glass comprising a glass substrate and a coating comprising a heat absorbing layer and a low emissivity layer substantially as hereinbefore described with reference to any one of Examples 1 to 9.
23. A multiple glazing unit comprising a pane of coated glass as claimed in any of the preceding claims in spaced parallel relationship with a second glazing pane.
24. A multiple glazing unit as claimed in claim 23 exhibiting a total solar heat transmission at least 15% less than its visible light transmission.
25. A multiple glazing unit comprising a pane of high performance solar control glass substantially as hereinbefore described with reference to any one of Examples 1 to 9.

Fig.1.

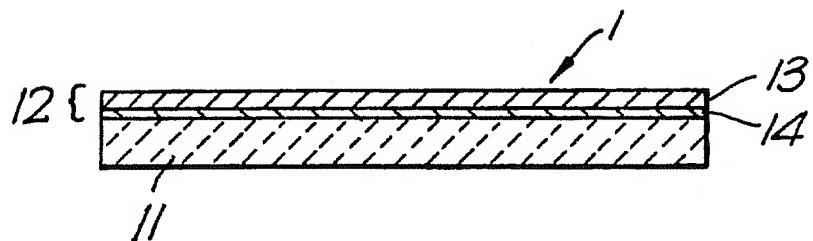


Fig.2.

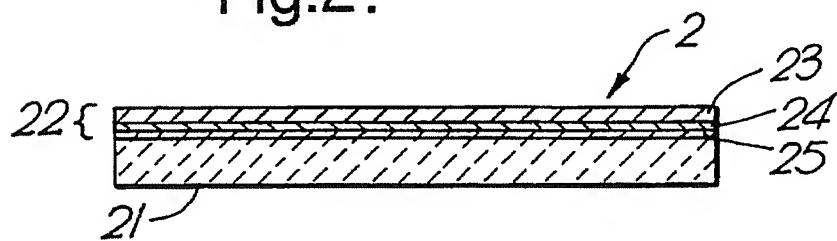
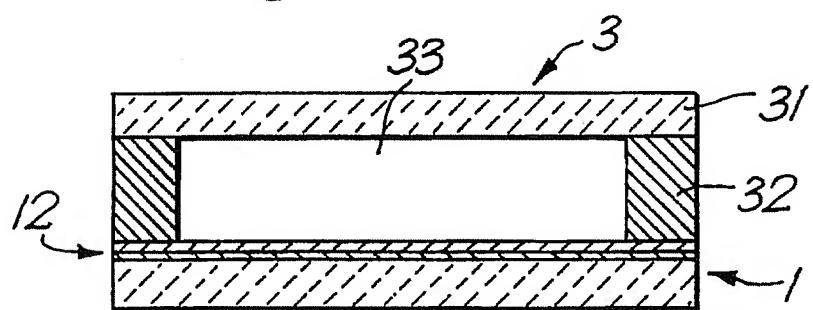


Fig.3.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02433

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C03C17/34

According to International Patent Classification(IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C03C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA 1 117 383 A (PPG INDUSTRIES INC) 2 February 1982 see page 3, paragraph 2 see page 9, paragraph 2 – paragraph 3	1-3, 7-13, 16, 18-25
Y	---	17
X	US 5 034 246 A (MANC ANDREW M ET AL) 23 July 1991 see column 2, line 10 – line 29 see column 3, line 35 – line 59 see column 7, line 35 – line 50	1-6, 10-13, 18-25
Y	---	17
		-/-

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

*** Special categories of cited documents :**

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

1

Date of the actual completion of the international search

3 December 1997

Date of mailing of the international search report

11/12/1997

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL – 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Van Bommel, L

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 97/02433

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 288 818 A (GLAVERBEL) 1 November 1995 see page 3, line 17 - page 8, line 7 -----	1-3, 7-12, 14-16, 18-25 17
A	US 5 004 490 A (BROWN FRANKLIN I) 2 April 1991 see column 3, line 25 - line 32 -----	1-3, 7-12, 14-16, 18-25
Y	US 5 168 003 A (PROSCIA JAMES W) 1 December 1992 see column 4, line 5 - line 36 see column 7, line 52 - column 8, line 8 -----	17
P,X	EP 0 735 009 A (CENTRAL GLASS CO LTD) 2 October 1996 see column 2, line 11 - line 27 see column 3, line 51 - column 5, line 5 -----	1-3, 7-12,14, 16,18-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 97/02433

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
CA 1117383 A	02-02-82	NONE		
US 5034246 A	23-07-91	DE 4125381 A	20-02-92	
		JP 4300212 A	23-10-92	
GB 2288818 A	01-11-95	BE 1009514 A	01-04-97	
		CZ 9501088 A	17-01-96	
		DE 19515015 A	02-11-95	
		FR 2719305 A	03-11-95	
		HU 70709 A	30-10-95	
		IT T0950296 A	27-10-95	
		LU 88606 A	01-09-95	
		NL 1000237 C	17-12-96	
		NL 1000237 A	27-10-95	
US 5004490 A	02-04-91	NONE		
US 5168003 A	01-12-92	CA 2068371 A,C	25-12-92	
		DE 69211444 D	18-07-96	
		DE 69211444 T	24-10-96	
		EP 0526966 A	10-02-93	
		JP 2510378 B	26-06-96	
		JP 5193993 A	03-08-93	
		KR 9610823 B	09-08-96	
		US 5271960 A	21-12-93	
EP 0735009 A	02-10-96	JP 8268732 A	15-10-96	